ABSTRACT

The contact angles of saturated calcium dodecanoate (CaC\textsubscript{12}) solution containing a second subsaturated surfactant on its precipitated surfaces were measured by using the drop shape analysis technique. The second subsaturated surfactants used were sodium dodecylsulfate (NaDS), sodium octanoate (NaC\textsubscript{8}), and nonylphenol ethoxylate nonionic surfactant (NPE). The results show that the second surfactants can act as a wetting agent. NaC\textsubscript{8} is the most effective wetting agent, while NPE is the least effective one. The graphical plot between contact angles and surfactant concentrations can be used in determination of the CMC value. Addition of NaCl can reduce the CMC of the anionic surfactant mixture of subsaturated NaDS and saturated CaC\textsubscript{12} solution by reducing electronic repulsion between surfactant molecules. The subsaturated NaDS system provides the highest effectiveness in spreading pressure and its value decreases with increase in NaCl concentration, while the subsaturated NPE system gives the lowest value. Different values of the critical surface tension obtained from the Zisman method of three subsaturated surfactants of NaDS, NPE, and NaC\textsubscript{8} were due to molecular structures and specific adsorption effects.

KEYWORDS
contact angle, subsaturated surfactant, wetting agent, spreading pressure

INTRODUCTION

The wetting of solid surfaces by liquids has great practical importance in many industrial processes, such as cleaning, printing, adhesion, and pesticide applications (Extrand, 2003). Improvement and modification of wettability are essential for technological applications of surfactant science. Addition of surface-active agents to water is a well-established means of enhancing the ability of aqueous solution to wet over solid surfaces by reducing both the surface tension of water and solid-water interfacial tension, as well as causing an increase in the value of spreading coefficient (Janczuk et al., 1998). During the past decade, spreading of surfactant solutions over solid surfaces has attracted considerable interest both in the academic world and in industry (Zhou et al., 2003). The ability to wet is a function of several parameters including the molecular structure of surfactant, its concentration, physical and chemical constitutions of each substrate and the environments.

In the most general sense, wetting is the displacement from a surface of one solid by another (Rosen, 1998). This phenomenon always involves three phases, at least two of which are fluids: a gas and two immiscible liquids, or a solid and two immiscible liquids, or a gas, a liquid, and a solid, or even three immiscible liquids. The most common method of evaluating wetting is contact angle measurements that date back to the early days of the 19\textsuperscript{th} century by Laplace and Young (Kabza et al., 2000). The closer the contact angle is to zero, the better the wetting is. Furthermore, the measurement of contact angles on a solid surface is the most practical way to obtain information about surface energy: solid-vapor and solid-liquid surface tensions (Kwok et al., 1997).
The contact angle is defined as the angle between the solid surface and the tangent to the surface of the drop at the point of contact of the two phases. For smooth and homogeneous surfaces its magnitude is given by the Young’s equation;

\[ \gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta \]  

which correlates the contact angle, \( \theta \), solid-vapor surface tension, \( \gamma_{SV} \), solid/liquid surface tension, \( \gamma_{SL} \), and liquid/vapor surface tension, \( \gamma_{LV} \). The various techniques are used for measuring contact angle, (Adamson, 1990) and the most commonly used method is sessile drop measurement (Hernainz and Caro, 2001) that measuring contact angle (\( \theta \)) directly from a drop of liquid resting on a flat surface of solid with goniometer scale or the contact angle may be obtained from a photograph of the drop profile as done in the previous work (Luangpirom et al., 2001) by taking the photograph of the droplet on the solid surfaces then determined the angle by computer program.

Study of the contact angles of saturated calcium dodecanoate (calcium soap precipitated) solutions on its precipitated surfaces was done by Balasuwatthi (2003). It was found that the second subsaturated surfactant solution of sodium dodecyl sulfate (NaDS) can act as an effective wetting agent in the system due to the reduction of the contact angle of saturated calcium dodecanoate solution on its precipitated surface as NaDS concentration increase until reaching the CMC of the mixture solution.

In this study, the effect of sodium chloride salt (NaCl) on the contact angle of saturated calcium dodecanoate (CaC\(_{12}\)) containing a second subsaturated sodium dodecyl sulfate solution on the precipitated surface of calcium dodecanoate, the effect of sodium octanoate (NaC\(_{8}\)), and also the effect of nonylphenol ethoxylate nonionic surfactant (NPE) on contact angles of saturated calcium dodecanoate solution on its precipitated surfaces were investigated in order to illuminate the primary wetting mechanism by relating results from contact angle, surface tension and surfactant adsorption experiments.

MATERIALS AND METHODS

The anionic surfactants, sodium dodecyl sulfate (NaDS) and n-octanoic acid sodium salt (NaC\(_{8}\)) both with 99+\% purity obtained from Sigma Chemical Co. (St. Louis, USA) were used without further purification. Nonylphenoxy poly(ethyleneoxy) ethanol, branched (NPE), EO group equal 9-10, and with 99+\% purity obtained from Rhodia Inc. (NJ, USA) was used as nonionic surfactant without further purification. Fatty acid used in this study was dodecanoic acid with 99+\% purity obtained from Sigma Chemical Co. (St. Louis, USA) was used to prepare calcium dodecanoate (CaC\(_{12}\)) precipitate. The precipitate obtained from the reaction was filtered and rinsed with distilled water and dried in an oven at 40\(^\circ\)C for 24 hours before crush with mortar. The fine powder of calcium dodecanoate precipitate was made in a pellet form by using hydraulic press (Bio-rad P/N 15011). Calcium chloride dihydrate (UNIVAR grade) were obtained from Ajax Chemical Co (Auburn, Australia). Sodium chloride and methanol both with AR grade were obtained from Lab-Scan Ltd. (Thailand). Doubly distilled and deionized water was used for preparation of solutions throughout these experiments. The saturated solution of calcium dodecanoate was firstly prepared after that the second subsaturated surfactant will be added in order to make the surfactant mixture solution.

The contact angle and surface tension were measured by using DSA drop shape analysis instrument (KRUSS Model DSA 10 Mk2, Germany). The sessile drop technique was used in contact angle measurement and the pendant drop technique was used for surface tension measurement. This apparatus consists of a computer, CCD camera and a closed chamber, which was connected to the temperature controller. For contact angle measurement, the solid precipitated surface was placed in the chamber and 10 \(\mu\)L of the surfactant solution droplet was introduced onto the surface using a micro syringe. The photographic pictures of droplets on the surfaces were captured by the camera, then the value of their contact angles were calculated from the drop profiles by using computer software. In case of surface
tension measurement, the liquid drop was produced from the tip of the syringe needle. The camera was
used to take the drop profile picture of the droplet while it was still attached to the needle. The values of
the surface tension were calculated from the drop profiles of the surfactant solution. The critical micelle
concentrations (CMC) were determined from a break point in plots of surface tension as a function of
bulk surfactant concentration.

For adsorption experiment, the surfactant solutions were added into vials containing solid CaC\textsubscript{12}
precipitate and allowed to equilibrate by shaking in a water bath at 30 \textdegree C for 4 days. After that, the
samples were centrifuged by a high-speed centrifuge (Sorval Super T21, Italy) at 3000 rpm before filtered
and then the supernatant solutions were analyzed for equilibrium surfactant concentrations by using
HPLC (Hewlett Packard series 1050, Avondale, USA) and UV-VIS spectrophotometer (Shimadzu 2550).

RESULTS

Contact Angle

The contact angles of a saturated CaC\textsubscript{12} solution containing subsaturated NaDS with varying salt concentration are shown in Figure 1. It was found that the contact angle decreased significantly with increasing NaDS concentration. The decrease of contact angle reached the plateaus at the NaDS concentrations of 7.0, 4.5 and 3.0 mM for the systems of 0.00, 0.01, and 0.03 M NaCl, respectively.

The contact angles of a saturated CaC\textsubscript{12} solution containing subsaturated NPE are shown in Figure 2. It was found that the contact angle decreased substantially from 90\textdegree to 60\textdegree with increase in NPE concentration and reached the plateau at the NPE concentration of 75 \textmu M.

The contact angles of a saturated CaC\textsubscript{12} solution containing subsaturated NaC\textsubscript{8} are shown in Figure 3. It was found that the contact angle decreased substantially (50\textdegree reduction) with increasing NaC\textsubscript{8} concentration until reaching the plateau at the NaC\textsubscript{8} concentration of 270 mM.

Liquid/Vapor Interfacial Tension

The critical micelle concentration (CMC) of the surfactant solution containing saturated CaC\textsubscript{12} and varying NaDS concentration were determined from the graphical plots between the liquid/vapor interfacial tension ($\gamma_{LV}$) and semi-logarithm of NaDS concentrations as shown in Figure 4. An intercept of the two tangents is the CMC value for each system. The CMC value was 8.0 mM for pure NaDS solution. In the mixture of saturated CaC\textsubscript{12} and subsaturated NaDS solutions,
the CMC values at 30°C were 7.0, 4.5, and 3.0 mM with 0.00, 0.01, and 0.03 M NaCl added, respectively.

The CMC of the pure NPE solution and the surfactant mixture between saturated CaC$_{12}$ and subsaturated NPE solution were also determined as shown in Figure 5. The CMC values were taken at 85 µM for the former and 75 M for the latter solutions.

Figure 6 shows that the CMC values were 280 mM for both pure NaC$_8$ solution and the mixture of saturated CaC$_{12}$ and subsaturated NaC$_8$ solution.

**Adsorption of Subsaturated Surfactant onto Precipitated Surfactant**

The adsorption isotherms of NaDS onto the surface of calcium dodecanoate (CaC$_{12}$) precipitate in the presence of various NaCl salt concentrations are shown in Figure 7. The adsorption reached the plateau when the NaDS concentration was around the CMC. In the vicinity of the CMC, the amount of NaDS adsorbed were 84, 77, and 71 µmole/g for the systems of 0.00, 0.01, and 0.03 M NaCl added, respectively.

The result in Figure 8 states that the adsorption of NPE increase with increase NPE concentration until reaching the plateau around 1.4 µmole/g of NPE adsorbed at the equilibrium NPE concentration of 75 µM, corresponding to the CMC value.

The adsorption of NaC$_8$ on the surface of CaC$_{12}$ precipitated in the saturated solution of CaC$_{12}$ encountered the problem in separation of the supernatant solution from the mixture of surfactant solution and the adsorbate. The solution was very slurry as the concentration of NaC$_8$ increase, due to not only C$_8$ ions in the surfactant solution tend to precipitate as CaC$_8$, but also dissolution of CaC$_{12}$ precipitate in the presence of Na$^+$ ions in the solution, when the ratio of calcium ion/octanoate ion exceed its K$_{sp}$ (K$_{sp}$CaC$_8$ = 4.53x10$^{-7}$ M$^3$ (Balasuwatthi *et al.*, 2004)). Sodium salts of both NaC$_{12}$ and NaC$_8$ have much higher...
solubility in aqueous solution than that of calcium salts.

**Calculation of Solid/Liquid Surface Tension**

Young’s equation (1), if the solid/vapor interfacial tension ($\gamma_{SV}$) and solid/liquid interfacial tension ($\gamma_{SL}$) were constant, the plot of $\cos \theta$ against $1/\gamma_{LV}$ should be linear with a slope equal to $\gamma_{SV} - \gamma_{SL}$. The deviation of the slope of the plot from linearity indicates that amount of surfactant adsorbed on the solid/liquid interface changes with varying surfactant concentration thereby changing in the value of solid/liquid interfacial tension. For the system of the subsaturated NaDS and saturated CaCl$_2$ (Fig. 9) with various NaCl concentrations, the results showed good correlation, however, it did not imply that the $\gamma_{SL}$ was constant with varying NaCl concentration. The results for the subsaturation systems of NPE (Fig. 10) and NaC$_8$ (Fig. 11) obviously show the deviation of the slope from linearity implying the change of $\gamma_{SL}$ with varying surfactant concentration.

Even though no method is presently available for directly measuring solid/liquid interfacial tension (Starkweather et al., 2000), eq. 1 can still be used to provide insight the interactions at solid/liquid interfaces by calculating $\gamma_{SL}$ relative to $\gamma_{SL}^0$ at a reference condition, which there is no second subsaturated surfactant. The difference of $\gamma_{SL}$ from the reference condition gives the spreading pressure, $\gamma_{SL}^0 - \gamma_{SL}$,

$$\gamma_{SL}^0 - \gamma_{SL} = \gamma_{LV} \cos \theta - \gamma_{LV}^0 \cos \theta^0$$

(2)

Rearrangement of equation (2) yields

$$\frac{(\gamma_{LV}^0/\gamma_{LV})(\cos \theta^0) - \cos \theta}{(\gamma_{LV}/\gamma_{LV})} = (\gamma_{SL}/\gamma_{LV})(\gamma_{SL}^0/\gamma_{LV})$$

(3)

The dependence of the spreading pressure for the solid/liquid interface indicates the reduction in surface tension induced by the adsorption of the subsaturated surfactants as...
shown for NaDS in Figure 12, for the surfactant mixture solution systems of NPE/CaC₁₂ in Figure 13 and NaC₈/CaC₁₂ in Figure 14. The spreading pressure increase with increase of the subsaturated surfactant concentration and plateauing at the CMC.

**Calculation of Critical Solid Surface Tension**

The Zisman plots of cosθ against γLV of the three different subsaturated surfactants (NaDS, NPE and NaC₈) are shown in Figures 15–17. The critical surface tension (γLV C) of the solid CaC₁₂ precipitate are 26.0, 13.7 and 20.0 mN/m for the system with subsaturated NaDS, NPE and NaC₈, respectively.

**DISCUSSION**

**Effect of subsaturated NaDS and NaCl salt**

The results of contact angle, surface tension, and adsorption measurements (Figs. 14 and 7) show that NaDS can act as an effective wetting agent by adsorbing at both liquid/vapor and solid/liquid interfaces. The value of contact angle in the vicinity of the CMC is about 40°, indicating that calcium dodecanoate precipitated surface is fairly hydrophilic in the presence of a second subsaturated surfactant. It implies that NaDS should adsorb by figuring their head groups out as already seen in the previous work (Balasuwaththi et al., 2004). The effect of NaCl salt addition to the system of the subsaturated NaDS and saturated CaC₁₂ on CaC₁₂ precipitate illustrated by the reduction in the liquid/vapor interfacial tension and the CMC of the mixture of the surfactant solution (Fig. 4) is due mainly to the decrease in the ionic atmosphere surrounding the ionic head groups in the presence of the additional electrolyte (Rosen, 1989). The increase in the amount of NaDS adsorbed with NaCl concentration should be due to the reduction in electronic repulsion between surfactant molecules. However, increased NaDS concentration also increases the amount of CaDS precipitation as
already seen in the previous work. As the micelle formation phenomenon takes place when the concentration of surfactant mixture solution is greater than mixed CMC, there is a mixed micelle which is composed of both the dodecyl sulfate (DS) and dodecanoate (C\textsubscript{12}) anionic surfactants. The higher the concentration of NaDS, the more the mixed micelles are formed. This occurrence causes some precipitated CaC\textsubscript{12} to dissolve, allows the dodecanoate to micellize, and causes some of the dissolved calcium ion (Ca\textsuperscript{2+}) to end up as unassociated in the solution. When the concentration of calcium ion is high enough until the ratio of calcium ion/ dodecyl sulfate ion exceeds its K\textsubscript{sp} (K\textsubscript{sp}\textsubscript{CaDS} = 2.65\times10\textsuperscript{-11} M\textsuperscript{3}, (Balasuwaththi et al., 2004)), the precipitation of dodecyl sulfate ion occurs as the calcium salt. The more NaDS added, the more CaC\textsubscript{12} dissolves and the more CaDS precipitates. Unfortunately, the solution depression method that determines the amount of NaDS adsorbed from the difference between the initial and final concentrations cannot distinguish the NaDS adsorption from the NaDS precipitation. Therefore, only the apparent adsorption of the surfactant was reported. Furthermore, the determination of the spreading pressure of the surfactant mixture between subsaturated NaDS and saturated CaC\textsubscript{12} solution (Fig. 12) shows that the spreading pressure decreases as NaCl concentration increases, which implies that the value of \(\gamma_{SL}\) does not decrease as the amount of NaDS adsorbed on the solid/liquid interface increases (Fig. 7). The depletion of NaDS in the solution to the solid surface is due not only to the NaDS adsorption, but also to the precipitation. This combination of adsorption and precipitation was defined as “abstraction” by Hanna and Somasundaran (1979). According to the linear slope obtained from the plot of \(\cos \theta\) against \(1/\gamma_{LV}\) based on Young’s equation (Fig. 9), the results confirms no change of \(\gamma_{SL}\) as NaDS adsorption increase at the solid/liquid interface due to the precipitation of DS’ with Ca\textsuperscript{2+} ions on the solid surface. However, the determination of the effect on the solid spreading pressure...
shows that NaDS provides the greatest spreading pressure compared with NPE and NaC₈ which are also used as second subsaturated surfactants.

**Effect of NPE nonionic surfactant**

The subsaturated NPE nonionic surfactant can also act as an effective wetting agent with 30° contact angle reduction. The mixed CMC (~75 µM) values obtained from both the surface tension (Fig. 5) and adsorption measurements (Fig. 8) agree well. However, in the case of polyoxyethyleneated nonionic surfactants, adsorption may produce a steric barrier (Rosen, 1989), due to its structure, i.e. branched molecular structure and also aromatic nucleus, caused looser packing of the surfactant molecules at the surface. The even stronger evidence for this assumption is the lowest effect on the solid spreading pressure compared with NaDS and NaC₈.

**Effect of NaC₈**

The effect of NaC₈ (Fig. 3 and Fig. 6) indicates that NaC₈ is the most effective wetting agent, which causes 50° contact angle reduction. The spreading pressure of NaC₈ increases with increasing in NaC₈ concentration at the low NaC₈ concentration range, the value decreases with the NaC₈ concentration higher than 100 mM, and tends to be constant at the CMC. This should be due to the NaC₈ adsorption playing a major role in decreasing the solid/liquid interfacial tension of the solid surface at low concentration until the precipitation phenomenon occurs.

**The critical solid surface tension**

Zisman has introduced an empirical procedure to estimate the wettability of solid surface (Siboni et al., 2004). A critical surface tension, γₛ, for the solid surface is defined as the surface tension of the reference liquid which fully wets the solid surface or the surface tension needed to give a zero contact angle on the solid.

Wetting enhancement by surfactants is commonly attributed primarily to a reduction in liquid/vapor surface tension (Balasuwatthi et al., 2004). Increasing adsorption of the
second subsaturated surfactant onto the CaC12 precipitate is the cause of the decrease in $\gamma_{SL}$, just as the second subsaturated surfactant adsorption at the liquid/vapor interface is responsible for the reduction in $\gamma_{LV}$ as the subsaturated surfactant concentration increases.

The Zisman equation is as follows:

$$\cos \theta = a + b\gamma_{LV}$$  \hspace{1cm} (4)

or

$$\cos \theta = 1 - \beta (\gamma_{LV} - \gamma_{LV}^{C})$$ \hspace{1cm} (5)

where $\gamma_{LV}^{C}$ is the critical surface tension characteristic of the solid. The Zisman plots of the experimental results obtained for NaDS/CaC12, NPE/CaC12, and NaC8/CaC12 (Figs. 19-21) show that the Zisman equation is not obeyed over the range of conditions studied. Evaluation of the linear region of the Zisman plot for the system of NaDS/CaC12 gives the value of critical surface tension, $\gamma_c$ of about 26 mN/m and $\beta = 0.028$ which are comparable with the results from the previous work, $\gamma_c = 25.5$ mN/m and $\beta = 0.045$ (Balasuwaththi et al., 2004). The addition of NaCl does not affect the value of the critical surface tension (Fig.19). For the NPE/CaC12 system, the critical surface tension is 13.7 mN/m and $\beta = 0.029$ and $\gamma_c = 20.0$ mN/m and $\beta = 0.019$ for the NaC8/CaC12 system. Similar results illustrating the distinction of the critical surface tension by using solutions were reported by Nylund and co-worker (1998), for a resin and a stainless steel surfaces with different liquids. They used diiodomethane and $\alpha$-bromonaphthalene as pure probe liquids and other solutions for the determination. They found that $\gamma_c$ was approximate 42.0 mN/m and 40.3 mN/m for the resin surface and the stainless steel surface, respectively by using the probe liquid, where as when using acetic acid solution, $\gamma_c$ were 25.4 mN/m for the resin surface and 23.7 mN/m for the stainless steel surface. They considered the discrepancy in this critical surface tension values as the result from specific adsorption effects. The differences in the results of CaC12 critical surface tension determined by using surfactant mixture solutions received from this work is due to the dissimilarity in the interactions of each surfactant mixture solution and the solid surface. The total surface tension of liquids and solids can be composed of sub-part of surface tension, i.e. polar parts of surface tension, disperse parts of surface tension, and hydrogen bonding parts of surface tension. The composition of these parts of surface tension for each substance depends on its the molecular structure. In the case of subsaturated surfactants NaDS, NPE, and NaC8, the molecular structure of each subsaturated surfactant as follows;

- NaDS : $\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{SO}_4\text{Na}$
- NPE : $\text{C}_{15}\text{H}_{24}\text{O(C}_2\text{H}_4\text{O})_n$ \hspace{1cm} $n = 9-10$
- NaC8 : $\text{CH}_3(\text{CH}_2)_5\text{COONa}$

NPE should have the highest van der Waals interaction as it has the largest hydrophobic portion while NaC8 with the shortest chain length should provide the lowest value. The polar part contribution to surface tension of NPE is hydrogen bonding mainly from EO groups ($n = 9-10$), which NaDS and NaC8, both an anionic and carry the same charge can have the contribution form the dipole-dipole interaction and Lewis acid-base interaction. Therefore, the second subsaturated surfactant which has different molecular structure from the others will interact differently on the solid precipitated of CaC12 surface. The linear relationship of Zisman plot only applies when the relationship between the disperse and polar interactions is the same between the solid and the liquid. This particular case occurs when a purely disperse interactive solid and liquid are involved. Therefore, only some ranges determined from the Zisman plot obey the linear relationship. This fact indicates that the use of solutions for determination of the critical surface tension is seldom acceptable and also illustrate the risk of using the Zisman equation beyond its original intention as Zisman seriously pointed out.
CONCLUSIONS

Determination of contact angle illustrates that the second subsaturated surfactants, i.e. NaDS, NPE and NaC₈ can act as effective wetting agents in the system of saturated CaC₁₂ solution on its precipitated surface. NaC₈ is the most effective wetting agent while NPE is the least effective one. The value of CMC determined from the plot between contact angle and subsaturated surfactant concentration in each surfactant mixture system gives the same value as obtained from the plot between surface tension versus surfactant concentration and surfactant adsorbed versus equilibrium surfactant concentration, which are general methods used in determination of CMC values. Addition of NaCl in the system of saturated CaC₁₂ and subsaturated NaDS decreases the CMC value of the surfactant mixture solution by decreasing of electronic repulsion between surfactant molecules. The difference between the molecular structure of each subsaturated surfactant and also the distinction in their composition of subparts of surface tension result in the specific interaction between the surfactant solution and the solid surface as can be observed from the dissimilar value of the critical surface tension of the CaC₁₂ solid surface by application of the Zisman equation with the surfactant mixture solutions.

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